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V. "On the Action of Dibromide of Ethylene on Pyridine." By JOHN DAVIDSON, Esq. Communicated by Dr. HOFMANN. Received May 24, 1861.

Pyridine, as is well known, has been obtained in the destructive distillation of coal, of certain varieties of shale, and of animal substances. The specimen with which I worked was obtained from coal-tar, and separated by distillation from the picoline: it boiled constantly at 118°.5 °C.

A mixture of pyridine and dibromide of ethylene gradually darkens, and at last becomes brown; no crystals, however, are deposited; on the other hand, the reaction proceeds with rapidity at 100° C. After the lapse of three hours the mixture is converted into an almost black crystalline mass, from which, by successive treatment with cold, and crystallization from hot, alcohol, a beautiful bromide, crystallizing in silky plates, is obtained. In preparing this bromide, it is advisable to add to the mixture of the anhydrous substances about one-fifth or one-sixth of its volume of alcohol, and to digest in sealed tubes. The whole liquid solidifies in this manner into a silky crystalline mass, which is only very slightly coloured.

The crystalline bromide is extremely soluble in water; I did not succeed in getting crystals from the aqueous solution. It is very soluble in boiling, but dissolves only slightly in cold alcohol; the boiling alcoholic solution solidifies on cooling into a pearly crystalline mass. Larger and transparent crystals may be obtained from dilute solutions, but in no case were their forms sufficiently perfect for determination. The simplest expression arrived at in analysing the bromide is the formula

but the mode of formation of the new compound unmistakeably shows that this expression must be doubled, and that the composition and weight of its molecule is represented by the formula

Pyridine, then, imitates triethylamine and triethylphosphine in their deportment with dibromide of ethylene, the new bromide being

\* 
$$H=1$$
;  $O=16$ ;  $C=12$ , &c.

formed by the union of one molecule of the latter with two molecules of pyridine,

$$C_2 H_4 Br_2 + 2 C_5 H_5 N = C_{12} H_{14} N_2 Br_2$$

The constitution of pyridine itself is but imperfectly made out. All we know is that this substance is a tertiary monamine; the nature of the radicals which replace the hydrogen is as yet uncertain. Pyridine, in accordance with our present knowledge, may be represented by the expression

and the molecular construction of the new bromide may be expressed by the formula

$$\left[ (C_2 H_4)^{\prime\prime} \frac{(C_5 H_5)^{\prime\prime\prime} N}{(C_5 H_5)^{\prime\prime\prime} N} \right]^{\prime\prime} Br_2.$$

The composition of the bromide is confirmed by the analysis of the chloride and platinum-salt.

Dichloride.—Treatment of the dibromide with chloride of silver yields the corresponding dichloride as a crystalline and extremely soluble substance, containing

$$C_{12} H_{14} N_2 Cl_2 = \left[ (C_2 H_4)'' \begin{array}{c} (C_5 H_5)''' N \\ (C_5 H_5)''' N \end{array} \right]'' Cl_2.$$

Platinum-salt.—The solution of the above salt yields with dichloride of platinum a pale yellow and apparently amorphous precipitate, insoluble in water and alcohol, and but slightly soluble in boiling concentrated hydrochloric acid, from which, on cooling, it almost entirely separates in small brilliant yellow plates, which were found to contain

$$C_{_{12}}\,H_{_{14}}\,N_{_{2}}\,Pt_{_{2}}\,Cl_{_{6}}\,=\,\left[(C_{_{2}}\,H_{_{4}})''\,\frac{(C_{_{5}}\,H_{_{5}})'''\,N}{(C_{_{5}}\,H_{_{5}})'''\,N}\right]''Cl_{_{2}},\,2\,Pt\,Cl_{_{2}}.$$

The solution of the dibromide, when mixed with freshly precipitated oxide of silver in the cold, furnishes a transparent colourless and powerfully alkaline liquid which contains the corresponding base, viz. the hydrate of ethylene-dipyridyl-diammonium,

$$C_{12} H_{16} N_2 O_2 = \frac{\left[ (C_2 H_2)'' \ 2(C_5 H_6)''' N_2 \right]''}{H_0} O_2.$$

The existence of this compound in the solution is readily proved by saturating with hydrochloric acid, and adding dichloride of platinum, when the pale yellow platinum-salt previously mentioned is precipitated. This salt was submitted to analysis.

The hydrates of the diatomic pyridine-derivatives are far less stable than Professor Hofmann's ethylated bases in the nitrogen- and phosphorus-series. Even at the common temperature, much more so by ebullition, the solution of the free base becomes pink, violet, and finally ruby-red, and deposits after some time a brown powder, a peculiar odour like that of the heliotrope being at the same time evolved. I have not examined more minutely the changes which the pyridine-compound thus undergoes.

The above experiments were performed in Dr. Hofmann's laboratory.

VI. "On a New Class of Organic Bases, in which Nitrogen is substituted for Hydrogen." By Peter Griess, Esq. Communicated by Dr. HOFMANN. Received May 24, 1861.

In a previous Note I have called attention to two new bodies produced by the action of nitrous acid upon the alcoholic solution respectively of aniline and nitraniline. Both substances\*,

Aniline derivative . . . . 
$$C_{12} H_{11} N_{3}$$
,  
Nitraniline derivative . . .  $C_{12} H_{3} (NO_{2})_{2} N_{3}$ 

are generated by the substitution of one equivalent of nitrogen for three equivalents of hydrogen in the original compounds.

In continuing my experiments on the replacement of hydrogen by nitrogen in organic bodies generally, I have not only succeeded in producing similar compounds from nearly all the basic derivatives of aniline, but have also obtained corresponding products from toluidine and anisidine. The following equation represents the formation of these compounds in the aniline-series:—

$$2\underbrace{\left(C_{n} H_{(n+1)} N\right)}_{\text{Two equivalents}} + HNO_{2} = \underbrace{C_{2n} H_{2n-1} N_{3}}_{\text{New compound.}} + 2H_{2}O.$$
Two equivalents
of aniline.

I do not at present venture to express an opinion regarding the constitution of these bodies; nevertheless their formation, their mutual relations, and their decompositions may in a measure be

\* 
$$H=1$$
;  $O=16$ ;  $C=12$ , &c.